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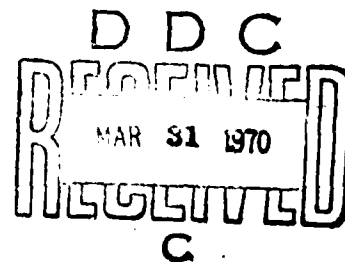
THE ADSORPTION OF
DINONYLNAPHTHALENESULFONATES
ON METAL OXIDE POWDERS

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The Adsorption of Dinonylnaphthalenesulfonates

on Metal Oxide Powders[1]

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The adsorption of oleophilic rust inhibitors, sodium and barium dinonylnaphthalenesulfonate, from cyclohexane solution on nickel(III) oxide and iron(III) oxide was investigated. Rate data for adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide indicate a complex mechanism of adsorption. An empirical equation was found that accurately describes the data. The log of the uncovered surface plotted against log time was linear. The extrapolated time for 50% coverage was 0.36 min. Experimentally the adsorption process was irreversible. The effect of temperature in the range of 10 to 60° on the adsorption isotherm was negligible. Adsorption isotherm data for sodium dinonylnaphthalenesulfonate were of a Langmuir type. The values of a indicated a more close-packed monolayer on nickel oxide than on iron oxide. The ratio of the molecules per square centimeter for the former and the latter was 1.49. The b values indicated a rather strong interaction at the metal oxide surfaces. Monolayer concentrations were found to be essentially the same irrespective of the salt used.

Introduction

High molecular weight petroleum sulfonates and synthetic sulfonates are receiving increasing military use as corrosion inhibiting additives for lubricants and hydraulic fluids. Dinonylnaphthalenesulfonates, in addition to being excellent corrosion inhibitors, approximate the petroleum sulfonates in structure and rust inhibiting properties and it is reasonable to assume that the adsorption characteristics of the petroleum sulfonates would be similar to the synthetic sulfonates.

Although the mechanism by which alkyl aryl sulfonates function as corrosion inhibitors is still unclear, several investigators have contributed to a better understanding of the corrosion inhibition mechanism by studying parameters affecting adsorption of sulfonate. For example, the presence of water was found to promote adsorption of calcium dinonylnaphthalenesulfonate on steel.[2] Shropshire recently observed that the degree of adsorption of petroleum sulfonates on calcium carbonate powder was determined by the history or method of preparation of the substrate.[3]

Smith, Gordon, and Nelson, in a study of the adsorption of calcium dinonylnaphthalenesulfonate at the gold–white oil interface, have reported that the adsorption is completely reversible and that the adsorbed monolayer is subject to displacement by a polyalcohol and poly(dodecyl methacrylate).[4] Because of the multiplicity of additives in lubricating fluids, the study of competitive reactions are particularly appropriate. We have found that the rust-inhibitive activity of petroleum sulfonates is affected by the choice of solvent; this indicates that the solvent is a parameter of considerable importance.

The purpose of this study was to investigate the adsorption characteristics of sodium and barium di-

(1) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) Van Hong, S. L. Eisler, D. Bootzin, and A. Harrison, *Corrosion*, 10, 343 (1954).

(3) J. A. Shropshire, *J. Colloid Interface Sci.*, 25, 389 (1967).

(4) M. L. Smith, B. E. Gordon, and R. C. Nelson, *J. Phys. Chem.*, 69, 3833 (1965).

nonylnaphthalenesulfonates. Since these materials are used in hydraulic systems that expose the lubricant to metal oxide surfaces, submicron iron(III) oxide and nickel(III) oxide powders were chosen as substrates. A low molecular weight hydrocarbon, cyclohexane, was used as a solvent. This investigation was undertaken to (1) study the rate of adsorption, (2) study the effect of temperature and dilution on desorption of sulfonate, (3) determine the concentration of sulfonate necessary to provide monolayer coverage, and (4) establish whether the adsorbed sulfonate is physisorbed or chemisorbed.

Experimental Section

Materials. The adsorbents (Vitro Laboratories, West Orange, New Jersey) were submicron iron(III) oxide and nickel(III) oxide powders with surface areas of 28 and 30 m²/g, respectively, as reported by the manufacturer[4] from the BET gas adsorption method. The powders were received in sealed containers. The powders were stored and handled under a nitrogen atmosphere. Cyclohexane (J. T. Baker Chemical Co., Instra-Analyzed grade) was the solvent in the adsorption studies. Batch analysis indicated 99.98% purity with a water content of 0.006%. The absence of polar impurities was periodically confirmed by the nonspreading characteristics of the solvent on a lycopodium seed film on distilled water.

Dinonylnaphthalenesulfonic acid (R. T. Vanderbilt Company, New York, N. Y.) was a 36% solution in heptane. The acid was purified with methanol according to the method reported by Kaufman and Singleterry.[5] The mixture readily separated into two phases; the upper phase, believed to contain resinous materials, was rejected. The sodium salt was prepared by neutralizing a solution of the acid with an excess of aqueous sodium hydroxide and subsequently back-titrating to the potentiometric end point. The solution was filtered and excess solvent removed by distillation at a reduced pressure. The salt was further purified by extracting its 2-propanol-water solution with petroleum ether. The barium salt was prepared by addition of re-precipitated barium hydroxide to a solution of the purified acid followed by back-titration to the potentiometric end point. Residual solvents were removed from the residue by several additions of cyclohexane during a distillation at reduced pressure. Both salts were dried at 60° and 15 μ. Triplicate analysis indicated that the sodium salt contained 4.73 ± 0.01% sodium (4.76% theory) and the barium salt contained 13.16 ± 0.02% barium (13.00% theory).

Adsorption Measurements. The adsorption of sulfonate on metal oxide powders was studied over the concentration range of 0.001 to 0.1%. In the adsorptive isotherm studies, 10 ml of cyclohexane-sulfonate solution was equilibrated with 500 mg of metal oxide in a small glass vial for 96 hr at room temperature. The

mixture was centrifuged; the completeness of the separation was readily ascertained by the Tyndal effect. Although the average particle size for the powder was 0.02 μ, ultraviolet analysis within the short wavelength range indicated analytically clean separations. Analytical determinations of equilibrium concentrations were made at 233 and 284 mμ with a Beckman DK-2 recording spectrophotometer with matching 1-cm silica cells. Surface coverage was calculated from the equilibrium concentration data. Data are presented in Table I and Figures 1-6.

Table I: Calculated Adsorption Equilibrium Values[a] for Sodium Dinonylnaphthalenesulfonate

	$K_{eq} \times 10^{14}$	
θ[b]	Ni₂O₃	Fe₂O₃
0.1-0.3	1.08	1.11
0.3-0.5	1.20	1.80
0.5-0.8	1.13	1.11
0.8-0.9	0.85	0.70
	0.57	0.58
0.9-1.0	0.73	0.86
	0.78	0.63

[a] Calculated from eq 4 in text. [b] Fractional surface area assuming a value of 1 for a monolayer.

In the study of the rate of adsorption of sodium sulfonate on nickel oxide, the initial concentration of the sulfonate was the minimum amount necessary to assure monolayer coverage on a specified amount of nickel oxide. The rate study was made at room temperature and the procedure was similar to that employed in the adsorption isotherm study. Each point in the rate curve (Figure 1) was determined from an independent sample.

The desorption study was essentially an investigation of the reversibility of the adsorption isotherm for sodium sulfonate on nickel oxide; 50 ml of 0.1984% sodium dinonylnaphthalenesulfonate in cyclohexane was equilibrated with 2.5 g of nickel(III) oxide for 24 hr; 25-ml aliquots were periodically withdrawn (8 to 16 hr) and replaced with an equal volume of pure cyclohexane. This study was made at room temperature. Concentrations of the diluted solution at equilibrium are given as a function of the number of dilutions in Figure 7. The effect of temperature on desorption or further adsorption was studied by a procedure similar to the adsorption isotherm procedure. Samples were equilibrated 2 hr at room temperature followed by 4 hr at various temperatures from 10 to 60°. The extent of the change in surface coverage was determined from identical samples kept at room temperature. The data are discussed later.
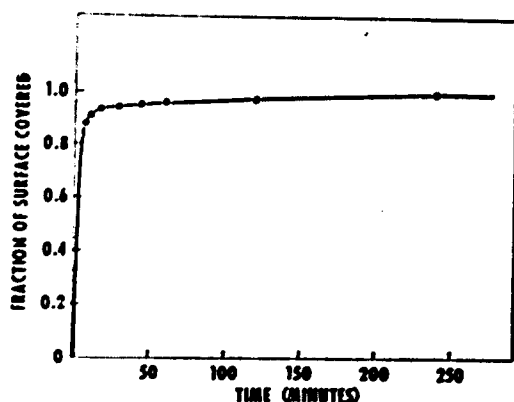
(5) S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, 12, 456 (1957).

Figure 1. Rate of adsorption of sodium dinonylnaphthalene-sulfonate on nickel oxide powder at room temperature.

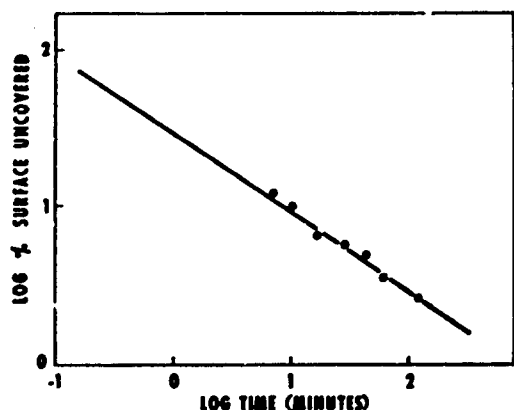Figure 4. Adsorption isotherms for barium dinonylnaphthalenesulfonate on iron and nickel oxide powder.

Figure 2. Fraction of surface uncovered vs. log time for the adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide powder.
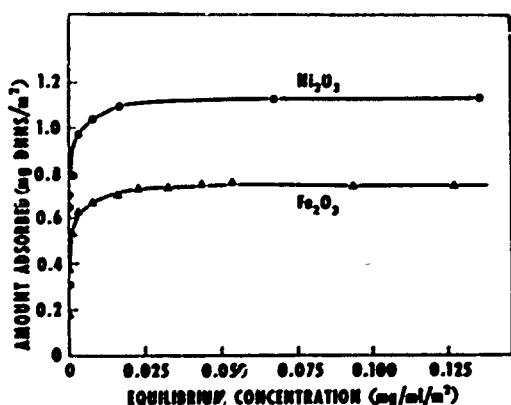

Figure 5. Langmuir plots for the sodium dinonylnaphthalene-sulfonate isotherms on nickel and iron oxide powders.

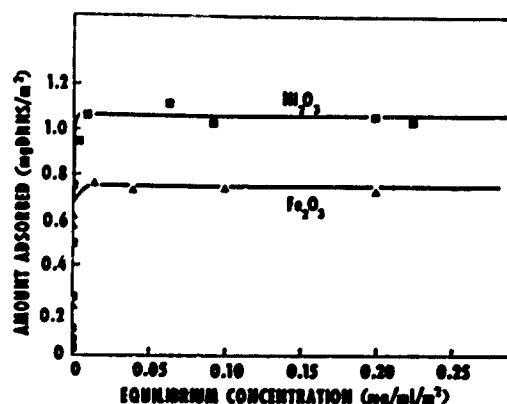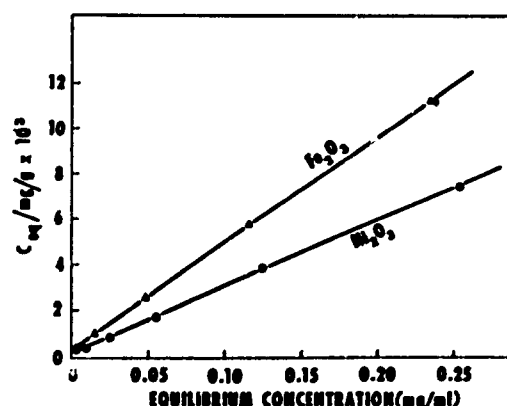Figure 3. Adsorption isotherms for sodium dinonylnaphthalenesulfonate on iron and nickel oxide powder.
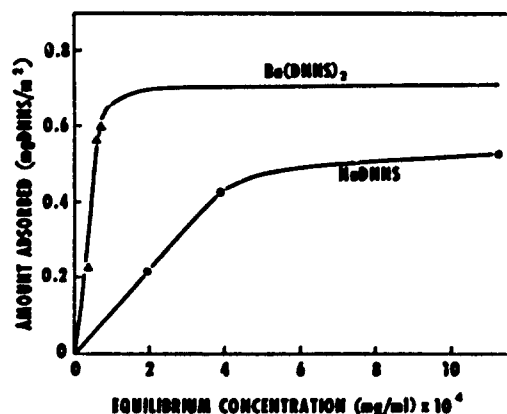

Figure 6. Expanded adsorption isotherms for sodium and barium dinonylnaphthalenesulfonate on iron oxide powder.

Results and Discussion

Adsorption Rate. The rapid rate of adsorption of sodium dinonylnaphthalenesulfonate on nickel(III) oxide in cyclohexane prevented measurements at low surface coverage values. The initial measurement at 7 min indicated that 0.88 monolayer was adsorbed, whereas 4 hr was required for the completion of the monolayer. The first value is within or slightly below the knee of the rate curve (Figure 1). The fractional

monolayer coverage values are slightly misleading since at full surface coverage the molecular packing is such that the long alkyl chains must be oriented perpendicular to the metal surface; however, at lower surface coverage, random orientation of the alkyl side chains is expected. Thus, at a coverage of 0.88 monolayer, the amount of surface available for adsorption is less than expected.

Although the data could not be fitted to any rate equations, an empirical equation was found that accu-
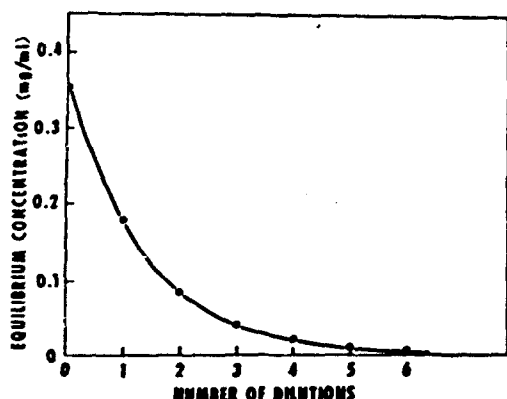
Figure 7. Effect of dilution on the equilibrium concentration of sodium dinonylnaphthalenesulfonate in the presence of nickel oxide.

rately described the data. The logarithm of the uncovered surface was found to vary linearly with the logarithm of time. The calculated time for 50% coverage was 0.36 min for adsorption (Figure 2). A second-order rate equation would be expected on the basis of the Langmuir adsorption theory; however, the logarithmic nature of the adsorption equation suggests a complex reaction.

The rapid asymptotic approach to a limiting value is probably associated with the low desorption rate of the sulfonate. The surface coverage obtained after 4 hr was within 0.2% of that obtained after 96 hr. In general, the rate curve resembles previously reported curves for similar materials. The rate curve for sodium dodecylbenzenesulfonate at the isooctane–steel interface[4] was characterized by a rapid approach to a high surface coverage value; however, the asymptotic approach to a limiting value was much slower. The reverse conditions were found by Smith, Gordon, and Nelson[4] for calcium dinonylnaphthalenesulfonate at the gold–white oil interface. Approximately 100 min was required for complete coverage but only 0.4 monolayer was rapidly adsorbed. This might indicate that the substrate plays an important role in determining adsorption rates.

Adsorption Isotherms. The adsorption isotherms for sodium and barium dinonylnaphthalenesulfonate in cyclohexane were determined on both iron(III) oxide and nickel(III) oxide. These data were normalized by a procedure similar to that used by Shropshire[3] in order to correct for variations in molecular weight and for the slight variation in the surface area of the substrates. These normalized data are graphically represented in Figures 3 and 4.

The isotherms for sodium dinonylnaphthalenesulfonate and barium dinonylnaphthalenesulfonate were characterized by a monotonic approach to a limiting adsorption. Adsorption data for sodium dinonylnaphthalenesulfonate on iron and nickel oxide powders were found to follow the Langmuir equation. This is

illustrated in Figure 5 where the ratio of the equilibrium concentration to the amount adsorbed is shown to be a linear function of the equilibrium concentration. The classical Langmuir equation can be expressed as

$$\frac{C}{x/m} = \frac{1}{ab} + \frac{C}{a} \qquad (1)$$

where C is the equilibrium concentration, x/m is the amount adsorbed per unit area, a is the maximum adsorption possible, and b is the ratio of the rate constants for adsorption and desorption. When the area of the substrate is known, a is a measure of the surface area occupied per molecule. The value of a was found to correspond to 68.4 Å^2/molecule for the sodium salt on nickel oxide and 109.1 Å^2/molecule for the sodium salt on iron oxide. It can be shown that these values correspond to a monolayer coverage. Reported data for the force–area relationship of calcium dinonylnaphthalenesulfonate[4-7] at the air–water interface has shown that the monomolecular film was of the liquid-expanding type. The maximum area per molecule was 200 Å^2; the minimum area for a tightly packed film was 125 Å^2 at 40 dyn/cm. It is reasonable to assume that the monovalent salt would occupy an area approximately half that of the divalent salt or an area of 62 to 100 Å^2 per molecule. Projections of Fisher-Hirschfelder-Taylor models of the dinonylnaphthalenesulfonate anion indicate that this assignment is reasonable. A study of the molecular models indicates that random orientation of the alkyl side chains probably predominates at low film pressures with the chains assuming a more oriented configuration with increasing pressure. Thus, the molecular packing of sodium dinonylnaphthalenesulfonate on nickel(III) oxide can be considered as close-packed, whereas the molecular packing on iron(III) oxide denotes a rather loosely packed monolayer. It is interesting to note that Smith and Allen[8] found a similar type of behavior for the adsorption of n-nonadecanoic acid at the nickel- and iron-cyclohexane interfaces. Molecular packing was considerably more close-packed on nickel than on iron.

The b term in the Langmuir equation expresses the ratio of the rate constants and has the dimensions of reciprocal concentration. The b value for sodium dinonylnaphthalenesulfonate was found to be 0.74 × 10^{-16} cm³/molecule for iron(III) oxide and 0.91 × 10^{-16} cm³/molecule for nickel(III) oxide. A slightly different mathematical treatment was employed to compare adsorption data for sodium dinonylnaphthalenesulfonate with that for barium dinonylnaphthalene-

(6) A. H. Roebuck, P. L. Gant, O. L. Riggs, and J. D. Sudbury, *Corrosion*, 13, 733 (1957).

(7) F. M. Fowkes, *J. Phys. Chem.*, 64, 1843 (1962).

(8) H. A. Smith and K. A. Allen, *ibid.*, 58, 449 (1954).

sulfonate. According to Laidler,[9] the rate of adsorption (γ_a) can be expressed as

$$\gamma_a = k_1 C_g C_s \tag{2}$$

and the rate of desorption (γ_d) as

$$\gamma_d = k_{-1} C_a \tag{3}$$

where C_g is the equilibrium concentration in solution (molecules/cm³), C_s is the concentration of adsorption centers (sites/cm²), and C_a is the concentration of adsorbed molecules (molecules/cm²). The equilibrium condition is given by equating these two rates

$$\frac{C_a}{C_g C_s} = \frac{k_1}{k_{-1}} = K_{eq} \tag{4}$$

where K_{eq} is an equilibrium constant for the system. The assumption was made that C_s was equal to the maximum number of molecules adsorbed per cm² less the number of molecules adsorbed per cm² at a given equilibrium concentration. These values are presented in Table I. Equilibrium constants at low surface coverage (less than 0.8 monolayer) were greater than the values at higher surface coverages. This can probably be attributed to initial adsorption at the most active sites or to the variety of spacial configurations available to an adsorbed molecule at low surface coverage. For example, the molecule could adsorb in a flat position and interact with a large number of sites. The heat of adsorption in the flat position would be larger than expected when the molecule is in a vertical configuration. The calculated equilibrium values (K_{eq}) are of the same order of magnitude as those calculated from the Langmuir equation. The slight discrepancy can be attributed to the assumption envolved in the calculation of C_s.

The adsorptive behavior of the barium salt differs considerably from the sodium salt in the region below the knee of the adsorption isotherm curve. This is illustrated in the expanded adsorption isotherms of sodium and barium dinonylnaphthalenesulfonate on iron(III) oxide (Figure 6). Data for the dinonylnaphthalenesulfonates on nickel(III) oxide are not included; however, graphic representation of these data is similar to those shown in Figure 6. The greater "adsorption" of the divalent cation is difficult to explain. The larger coordination sphere of the divalent cation might allow greater interaction with surface hydroxyl groups. Another possible explanation may be related to the stability and size of the barium and sodium dinonylnaphthalenesulfonate micelles. Kaufman and Singleterry[5,10] have reported differences in the micellar nature of these materials.

Molecular packing in the completed monolayer was found to be a function of the substrate; however, the cation does not appear to influence molecular packing. On nickel oxide, the monolayer concentrations were

1.12 ± 0.02 mg (DNNS)⁻/m² and 1.07 ± 0.04 mg (DNNS)⁻/m² for the sodium and barium salts, respectively. Slightly better agreement was obtained on iron oxide. The monolayer concentrations were 0.75 ± 0.01 and 0.74 ± 0.03 mg (DNNS)⁻/m² for the sodium and barium salts, respectively. This suggests that the monolayer might be considered as a close-packed array of anions with the cation in close proximity to provide electrical neutrality. The density of the packing indicates that the anions are in a configuration perpendicular to the surface. This configuration would allow maximum overlap of the filled p orbitals of the oxygen with vacant d orbitals of the metal atoms on a clean metal oxide surface. Interatomic distances for nickel metal are known to be 2.49 and 3.52 Å. It is interesting that the first value approximates the spacing in the sulfonate group itself. Other possible mechanisms for adsorption might include interaction of adsorbed water or surface hydroxyl groups with the coordination sphere of the cation or direct interaction of oxygen sites with the cation.

When determinations of monolayer concentration were made in relatively concentrated solutions, a slight but gradual decrease in the amount adsorbed was noted. The accuracy of these values is open to question since the sensitivity of the method decreases with increasing concentration; however, others[11] have noted a maximum in the adsorption isotherm for sodium dodecylbenzenesulfonate on nickel.

Effect of Temperature. The temperature dependence of the adsorption data for sodium dinonylnaphthalenesulfonate on nickel oxide was determined for possible elucidation of the interaction at the metal oxide surface. For example, if the data showed a strong dependence on temperature, it would be reasonable to attribute adsorption to van der Waals forces or other interactions such as intermolecular cohesion or hydrogen bonding to surface hydroxyl groups. (Chemically bound water appearing as hydroxyl groups on α-Fe₂O₃ surfaces is suggested by the work of Jurinak.[12]) At elevated temperatures of 45 and 60°, no detectable desorption was found at a surface coverage of 0.28 monolayer. At 60°, the amount desorbed at surface coverage of 0.95 and 1.00 monolayer was 1.1 and 1.4%, respectively. The data support a monolayer consisting essentially of chemisorbed species. The data are reasonable when the micellar nature of sodium dinonylnaphthalenesulfonate is considered. In effect, the metal oxide and micelle are both competing for adsorption of the monomer, and in the absence of a strong interaction at the

(9) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, N. Y., 1950, p 150.

(10) S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **10**, 139 (1955).

(11) A. Fava and H. Eyring, *J. Phys. Chem.*, **6C**, 890 (1956).

(12) J. J. Jurinak, *J. Colloid Sci.*, **19**, 477 (1964).

metal oxide surface, the monomer would be expected to re-enter the micelle phase.

Although the interaction at the metal oxide surface would be better evaluated by data on the isosteric heat of adsorption, the magnitude of the changes in concentration did not warrant exact calculations. Rough calculations indicated that the heat of adsorption was of the same order of magnitude as that found with chemical reactions.

Desorption Studies. The reversibility of the sodium dinonylnaphthalenesulfonate–nickel(III) oxide isotherm was investigated at room temperature (Figure 7). The initial amount of material adsorbed corresponded to full monolayer coverage and each dilution represented withdrawal of one-half of the volume of the supernatant liquid and the replacement with the same volume of clean cyclohexane. The equilibrium period was 24 hr; withdrawals were made after equilibration periods of 8 to 16 hr.

No significant desorption was found after six successive dilutions. This data indicate the absence of a significant fraction of easily desorbable sulfonate in the monolayer. Desorption undoubtedly must occur in order to reestablish equilibrium conditions; thus, the rate of desorption must be extremely slow. In order to better evaluate the rate of desorption, one equilibrium period was extended to 64 hr; however, no detectable desorption was noted.

Structural Considerations. Dinonylnaphthalenesulfonic acid is prepared by alkylation of naphthalene with nonene-1 which is made by the trimerization of propylene. Smith, *et al.,*[4] reported that dinonylnaphthalene is greater than 95% dialkylated and that the two nonyl groups are substituted in the same ring, which is different from that containing the sulfonate group. The sulfonic acid group is probably in an α position in view of the low temperature of sulfonation. Factors affecting the structure of the alkyl side chains include (1) the method of preparation of the nonenes (6 possible branch chained isomers) and (2) isomerization. The latter reaction is known to prevail in this type of alkylation[13] and attachment of the alkyl group would be expected at a tertiary carbon. Consideration of the structure of the nonene isomers and their most probable point of attachment indicates that the alkyl side chains are rather short and very highly branched. The structure of dinonylnaphthalenesulfonate may be more closely related to its corrosion-inhibiting ability than normally realized.

(13) A. C. Olson, *Ind. Eng. Chem.*, **32**, 833 (1960).

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13. ABSTRACT

The adsorption of oleophilic rust inhibitors, sodium and barium dinonylnaphthalenesulfonate, from cyclohexane solution on Nickel(III) oxide and iron(III) oxide was investigated. Rate data for adsorption of sodium dinonylnaphthalenesulfonate on nickel oxide indicate a complex mechanism of adsorption. An empirical equation was found that accurately describes the data. The log of the uncovered surface plotted against log time was linear. The extrapolated time for 50% coverage was 0.36 min. Experimentally the adsorption process was irreversible. The effect of temperature in the range of 10 to 60° on the adsorption isotherm was negligible. Adsorption isotherm data for sodium dinonylnaphthalenesulfonate were of a Langmuir type. The values of a indicated a more close-packed monolayer on nickel oxide than on iron oxide. The ratio of the molecules per square centimeter for the former and the latter was 1.49. The b values indicated a rather strong interaction at the metal oxide surfaces. Monolayer concentrations were found to be essentially the same irrespective of the salt used.

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